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SAMPLE PREPARATION OF METAL ALLOYS  
BY ELECTRIC DISCHARGE MACHINING

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16. Abstract <p>Electric discharge machining was investigated as a noncontaminating method of comminuting alloys for subsequent chemical analysis. Particulate dispersions in water were produced from bulk alloys at a rate of about 5 mg/min by using a commercially available machining instrument. The utility of this approach was demonstrated by results obtained when acidified dispersions were substituted for true acid solutions in an established spectrochemical method. The analysis results were not significantly different for the two sample forms. Particle size measurements and preliminary results from other spectrochemical methods which require direct aspiration of liquid into flame or plasma sources are reported.</p>			
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# SAMPLE PREPARATION OF METAL ALLOYS BY ELECTRIC DISCHARGE MACHINING

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## SUMMARY

With ever increasing use of automation in chemical analysis, the problem of dissolving corrosion-resistant alloys to prepare them for the analysis is fast becoming the time-limiting procedural step. Electric discharge machining was investigated as an approach to solving this problem. A commercially available instrument was used to perform a noncontaminating comminution of alloys to produce particulate dispersions in water at a rate of about 5 milligrams per minute. The particle size distributions of these dispersions were determined from the settling rate of the particles by Stokes' law. Other observations of particle characteristics were made by scanning electron micrography.

Chemical analyses of the dispersions were performed to evaluate the utility of this approach to sample preparation. The dispersions were acidified and analyzed by an established spectrochemical procedure developed to accommodate true solutions. The results were compared with results obtained from a concurrent analysis of the same nickel alloy in a true acid solution; the results for the two sample forms were not significantly different. Preliminary results also indicated the feasibility of analyzing these dispersions by other spectrochemical methods which require direct aspiration of liquids into flame or plasma sources.

## INTRODUCTION

The problem of sample preparation becomes more prominent as automation in the analytical chemistry laboratory increases. For as automation reduces the time required to perform a chemical analysis, the time-limiting step in the procedure often becomes the transformation of the as-received specimen into a form required by the analytical method. This operation often involves acid dissolution of materials that may not dissolve

easily and therefore requires so much time and effort as to constitute a major portion of the analysis cost. Unfortunately, automation has not yet been applied as successfully to solving the problems of solid sample preparation as it has been to expediting the subsequent steps in the analysis.

The problem can be illustrated with an example from the analytical laboratory at the Lewis Research Center, where an automated procedure for spectrochemical analysis has been developed and put to practical use (ref. 1). In this procedure, microgram amounts of sample material in acid solutions are dried on carbon anodes. The residue is then vaporized into an argon arc and analyzed spectroscopically. This method is applicable to a wide variety of sample compositions; however, it requires, as do many other methods of chemical analysis, that the sample be put in liquid form. This cannot always be done easily by conventional chemical means, especially when the sample is a material which has been deliberately synthesized to resist corrosion. The need to analyze aerospace superalloys, products of corrosion research, and other corrosion-resistant materials by using an analytical system requiring the sample in liquid form motivated this search for an improved sample preparation procedure.

This study was undertaken to determine whether it would be possible to produce, without complete acid dissolution, a liquid form of a metallic specimen that would be a suitable sample for analytical systems designed to accommodate solutions. The approach described in this report was to produce a particulate dispersion of the specimen by comminution by using a commercially available instrument designed for electric discharge machining (EDM). The dispersions were intended to be volumetrically manipulated and utilized in subsequent analytical applications in much the same manner as true solutions.

A previous attempt to produce metallic dispersions with a spark discharge under water is described in reference 2. The spark source used was similar to that used in spectroscopic excitation with stainless steel rod specimens used as self-electrodes. Our attempts to reproduce these results were unsuccessful because of the difficulty encountered in maintaining the critical spark gap spacing required to sustain the spark discharge under water. The electrodes tended to weld together or erode away and thus caused the discharge to be extinguished after only a few seconds of operation. However, the EDM instrument used in our work incorporated electronic control of the spark gap spacing and was well suited for producing dispersions of metals in liquids routinely.

The dispersions produced in this investigation were evaluated to determine their suitability for use as samples in spectrochemical analyses. The evaluation consisted of determining the particle size distributions, making qualitative observations of some of the physical and chemical characteristics of the dispersed material, and analyzing the dispersions in each of three spectrochemical analysis systems.

## MATERIALS, APPARATUS, AND PROCEDURE

### Sample Materials

The dispersions evaluated in this study were produced in water from high-temperature nickel-base superalloys, which tend to resist corrosion. Three such alloys were used in evaluating the sample preparation procedure under study. These were an experimental NASA nickel alloy, called MCrAl; a modified version of NASA-TRW VI A produced by casting; and a modified version of NASA-TRW VI A produced by powder metallurgy techniques. A fourth nickel alloy, Hastelloy C, was used to optimize the EDM spark power setting.

### Sparking Procedure

Spark machine. - A commercially available Servo-Met electric discharge machine was used to produce metallic dispersions in liquid media. The machine is designed to produce a spark discharge in a dielectric liquid at a direct-current breakdown potential between 50 and 200 volts. The spark discharge power can be chosen by selecting any one of the seven combinations of resistance  $R$  and capacitance  $C$  shown in table I. These determine the  $RC$  of the circuit that is block diagrammed in figure 1. The capacitor charges at a rate determined by the resistor until the dielectric breakdown voltage is reached, when a spark discharge takes place. The capacitor is recharged through the resistor, and the cycle is repeated. The breakdown voltage is proportional to the gap spacing, which is controlled to close tolerance by a servomechanism coupled to the cathode. This feature allows continuous unattended operation over the required period of time. A small vibrator mounted on top of the servomechanism head was used to mini-

TABLE I. - CIRCUIT VALUES FOR FIGURE 1

Power setting	Resistance, R, ohms	Capacitance, C, $\mu\text{F}$	Time constant, RC, $\mu\text{sec}$
1	27	30	810
2	43	6	258
3	108	1	108
4	235	.25	58.8
5	420	.05	21
6	1000	.01	10
7	8200	$10^{-5}$	.082

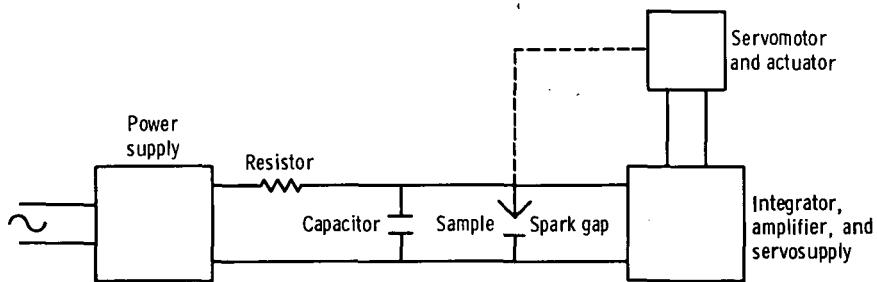


Figure 1. - Circuit block diagram of electric discharge machine.

mize further contact welding during the machining operation.

Sample holding hardware was fabricated from copper, an element not of interest in this work, and was used in the arrangement with the spark discharge machine shown in figure 2. The sample holders, beaker, and specimens were scaled according to a sample volume of approximately 25 cubic centimeters.

Operational procedure. - To produce metal dispersions, two pieces of the specimen, nominally 2 by 2 by 25 millimeters, were cleaned, weighed, and mounted in the electrode holding hardware as shown in figure 2. The mounted electrode pair was then submerged

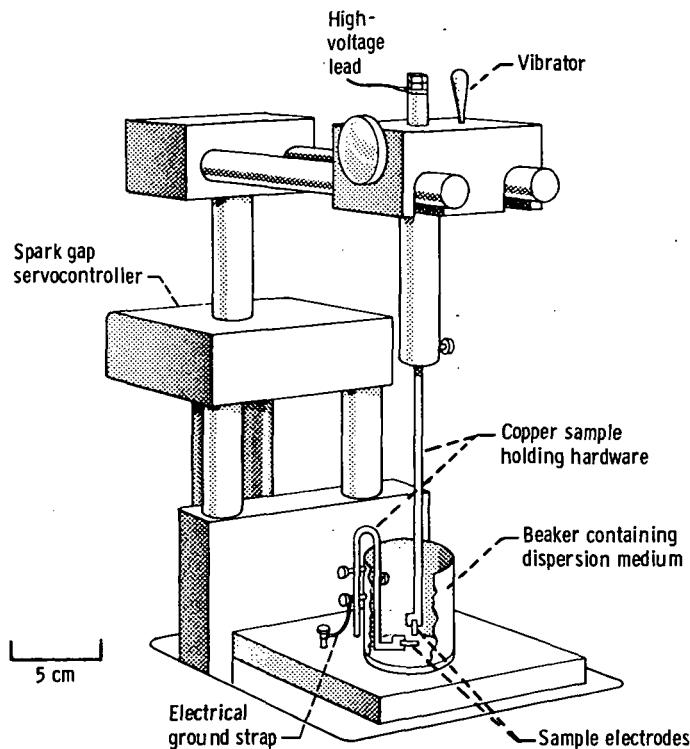


Figure 2. - Schematic diagram showing adaptation of electric discharge machine to dispersion production in water.

in the dispersing medium, and the discharge initiated with the vibrator in operation. The EDM process was terminated after a period of time determined by the machining rate. The amount of metal in the dispersion was estimated by the weight loss of the electrode pair. Dispersions from four nickel alloys were produced in water for evaluation in this study.

### Particle Sizing and Characterization

Particle size distributions of dispersions of a nickel alloy were determined by using the Stokes formula for settling of spherical particles in liquid media:

$$r = \left[ \frac{9v\ell}{2T(\rho_1 - \rho_2)g} \right]^{1/2} \quad (1)$$

here

particle radius, cm

viscosity of medium, (g)(sec<sup>-1</sup>)(cm<sup>-1</sup>)

distance settled, cm

T time of settling, sec

$\rho_1$  density of particle, (g)(cm<sup>-3</sup>)

$\rho_2$  density of media, (g)(cm<sup>-3</sup>)

g gravitational acceleration, (cm)(sec<sup>-2</sup>)

For a settling distance of 1 centimeter in a water medium, the equation is

$$r = \left[ \frac{0.09 \ell}{2T(\rho_1 - 1)980} \right]^{1/2} \quad (2)$$

Figure 3 is a graph of particle diameter against settling time, according to equation (2), for aluminum (Al), nickel (Ni), and tungsten (W). Of these three metals, Al and W represent the extremes in density, and Ni represents the most abundant metal in the dispersions.

Particle size distributions were estimated in duplicate, by using the Stokes method, for dispersions prepared from a nickel alloy at both a higher and lower spark power. This was done by initially agitating the dispersion and allowing the material to settle for measured increments of time between 10 and 10<sup>5</sup> seconds. At each time increment

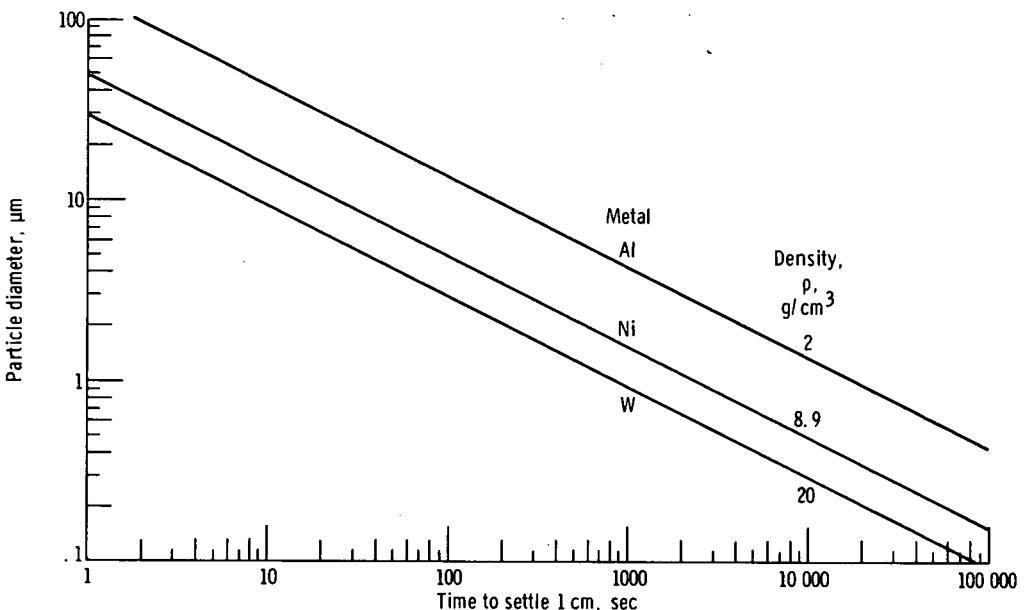


Figure 3. - Settling times predicted by Stokes' law for spherical particles in water (eq. (2)).

a 0.05-cubic-centimeter ( $50-\mu\text{l}$ ) aliquot was withdrawn from a region about 1 centimeter below the liquid surface by using a micropipette. The pipetted material was transferred to an aluminum weighing pan, dried at  $150^{\circ}\text{C}$ , and weighed to within about 1 microgram. The mass of each incremental weighing was then expressed as the mass fraction of the material initially suspended in the 0.05-cubic-centimeter ( $50-\mu\text{l}$ ) aliquot when the dispersion was fully agitated. The maximum spherical diameter of the particles in each incremental mass fraction was determined by equation (2). These data were plotted on log-probability paper, in accordance with the convention in particle size analysis, and are shown in figure 4.

Scanning electron micrographs were obtained on sample dispersions to aid in characterization.

#### Spectrochemical Analysis of Particulates

The dispersions were analyzed spectrochemically to determine their suitability for use as samples in each of three spectrochemical methods. Analyses of dispersions by emission spectroscopy were done by using a direct-current arc in argon buffered with silver chloride (AgCl) contained in the carbon anodes. The procedural details for this method are described in reference 1. In addition, preliminary data were obtained by the flame atomic absorption method and the inductively coupled plasma (ICP) method (ref. 3), wherein direct aspirations of dispersions into the flame and plasma were performed.

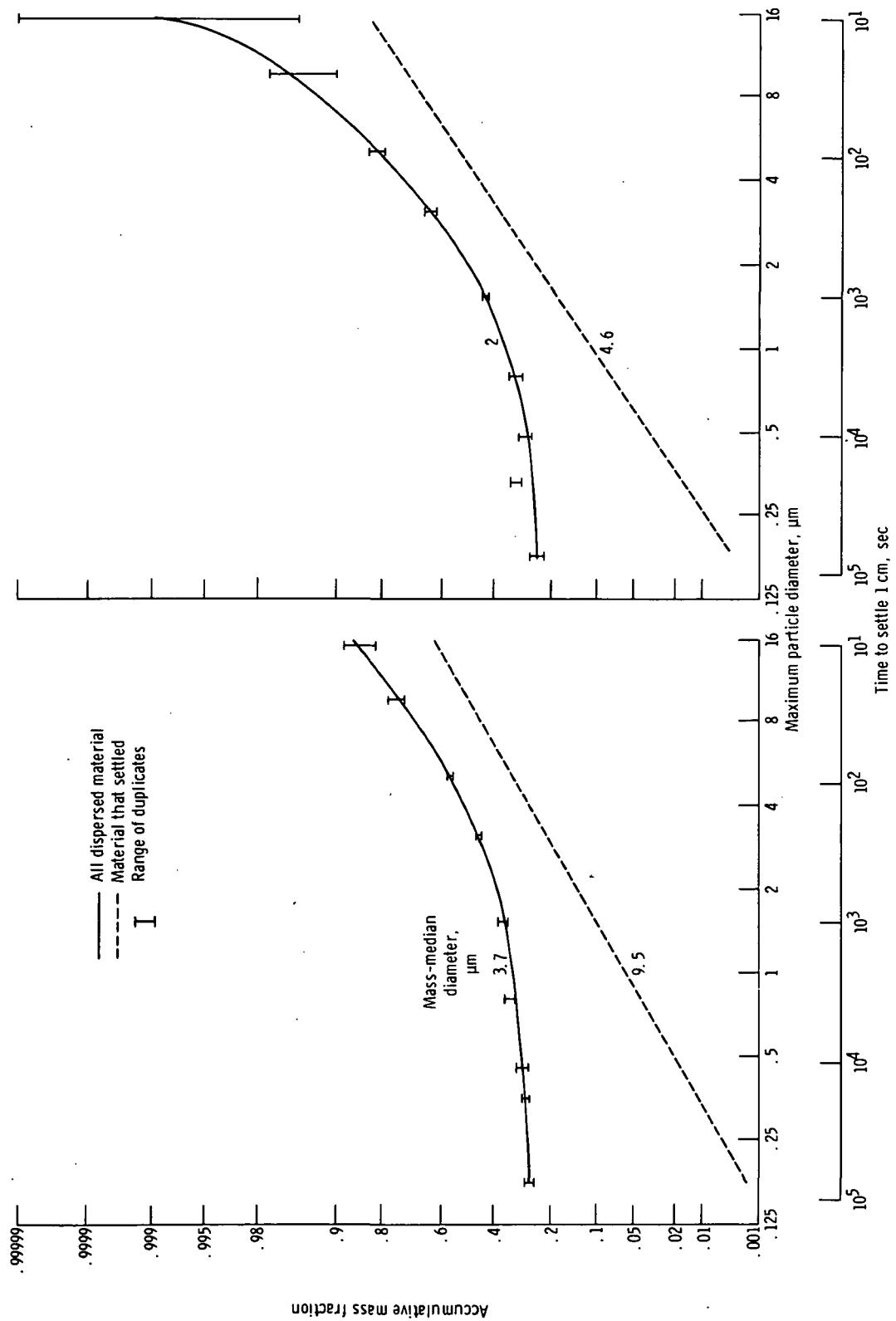


Figure 4. - Particle size distribution in dispersion prepared from nickel alloy by EDM in water.  
 (a) Power setting, 3.  
 (b) Power setting, 6.

Arc-excited emission. - In the arc-excited procedure, the water dispersions of the nickel alloys were acidified by adding about 10 percent of a concentrated mixture of 3 parts hydrochloric acid, 2 parts hydrofluoric acid, and 1 part nitric acid. Immediately after shaking, a 0.01-cubic-centimeter ( $10\text{-}\mu\ell$ ) aliquot was dosed onto carbon anodes containing the AgCl and dried at  $150^{\circ}\text{C}$ . The electrodes were then subjected to an argon arc discharge according to the procedure of reference 1. The emission data were converted to metal concentrations (in percent) by means of calibration functions established from single metal elements in acid solutions. These concentrations, obtained from the analysis of the dispersed material, were compared with those obtained from a concurrent analysis of the same nickel alloy specimen in a true acid solution.

A statistical test was applied to the comparison of the two sets of analytical results to determine if they differed significantly. The two-tailed t-test was used (ref. 4) to compare the concentration means, as if they were from two sets of data having the same standard deviation. The deviation from the acid solution analysis  $t$  was computed for each element by

$$t = \frac{D - A}{RMSE} \quad (3)$$

where

D element concentration mean from analysis of EDM dispersion, percent

A element concentration mean from analysis of acid solution, percent

RMSE root-mean-square error of analytical system, percent

The RMSE, the true capability of the system to resolve concentrational difference, is defined by

$$RMSE = \left( S^2 + \frac{N}{N - 1} E^2 \right)^{1/2} \quad (4)$$

where

S standard deviation, concentration percent

N number of replicates

E systematic error, concentration percent

The value of the level of significance was estimated by using  $N$  and the computed values of  $t$  with the curve of the  $t$  distribution (fig. 5) from reference 4. A  $t$  value greater than 2 yields (for  $N = 5$ ) a probability of significant difference greater than 0.9 and is interpreted to indicate a significant difference between the means.

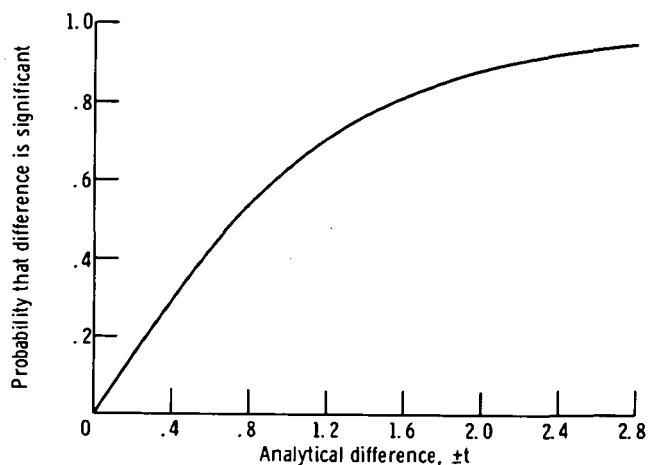


Figure 5. - Distribution of analytical difference for five replicates (ref. 4).

Atomic absorption. - In the atomic absorption experiments, the flame source was a laminar flow nitrous oxide burner with a 5-centimeter by 0.5-millimeter slot. The dispersions were aspirated while the plastic container was hand agitated. Absorbance measurements were made to estimate repeatability, concentration, and concentrational sensitivity for several elements in a nickel alloy.

Inductively coupled plasma. - The experiment with the ICP involved several aspirations only to establish feasibility of delivering EDM particles directly into the plasma. The aspiration system of the plasma was the same as that described in reference 3.

## RESULTS AND DISCUSSION

The successful application of EDM to the problem of preparing samples for chemical analysis depends upon a number of factors. These together with the results obtained are summarized in this section.

## Machining Rates

The rates of material removal by EDM cannot be stated in precise terms because of the difficulty in specifying all of the relevant parameters. The erosion rates are dependent on the spark power, liquid dielectric, and thermal and physical properties of the workpiece. The erosion rates also apparently change during the machining process. We obtained machining rates for the modified NASA-TRW VI A nickel alloy. The material was formed into electrodes approximately 2 by 2 millimeters on the sparking surface. The rates were between 6 and 8 milligrams per minute for a capacitance of 1 microfarad (power setting of 3 in table I) and between 1 and 3 milligrams per minute for a capacitance of 0.01 microfarad (power setting of 6). The gap voltage during these experiments fluctuated widely between about 50 and 200 volts, and it was not possible to record a meaningful value. Nevertheless, we believe these rates to be typical within about a factor of 2 for nickel alloys in water with the conditions described. These rates are about one-twentieth of the achievable machining rates in oil.

## Particle Sizes and Chemistry

Data derived from aliquot weighings for incrementally increasing settling times were plotted on a probability scale as a function of the particle diameter calculated from equation (1) and are shown in figure 4. A second abscissa scale shows the time required for a particle of corresponding size to settle 1 centimeter. For particles that were log-normally distributed, the plots are linear. Deviations from linearity of these data are due to the particles that were in suspension and did not settle according to equation (1). The mass fraction of these suspended particles is indicated by the ordinate value that the lower part of the curve approaches asymptotically. When this suspended mass is subtracted from the curves, a linear plot (the broken line) results. About 25 percent of the total solid particulates was in a suspension which settled by only a few percent over a 24-hour period. Evidence that this fraction of the mass consisted of suspended particles rather than dissolved material can be seen in table II. Virtually all of the suspended material could be removed by filtration through a pore size of 2 nanometers.

The effective mass-median diameters were estimated and are shown in figure 4 for the nonlinear and linear representations. The material produced at the lower power (setting of 6) was of smaller mass-median diameter and also had a somewhat narrower distribution, as indicated by the greater slope.

The effective particle number density as a function of particle diameter can also be estimated from the weights obtained at various settling time intervals. These estimates assume that the particles which settle are spherical. Two such estimates are shown in figure 6. They are for dispersions produced from the powder metallurgy version of the

modified NASA-TRW VI A alloy at power settings of 3 and 6. A typical scanning electron micrograph of dispersion particulates produced from the same nickel alloy at the lower power (setting of 6) is shown in figure 7. The impression obtained from viewing many of these micrographs is of a large number of particles of extremely small dimensions. Since the particle number density is proportional to the probability of observation in the

TABLE II. - RETENTION BY 2-NANOMETER FILTER OF EDM  
DISPERSION PRODUCED IN WATER AT POWER SETTING OF 6

Alloy composition		Spectrochemical analyses		Filter retention ratio, percent
Element	Concentration, percent	Suspension, mg/1000 cm <sup>3</sup>	Filtrate, mg/1000 cm <sup>3</sup>	
Aluminum	4.96	64	<0.05	>99.9
Cobalt	7.63	82	.4	99.5
Chromium	5.65	70	<.05	>99.9
Hafnium	.52	15	<.05	>99.6
Molybdenum	1.96	23	<.05	>99.7
Niobium	.55	9	<.05	>99.4
Nickel	63.27	704	1.7	99.7
Tantalum	9.12	104	.5	99.5
Titanium	1.04	16	<.05	>99.7
Tungsten	5.04	48	<.05	>99.8
Zirconium	.12	3	<.05	>98.3

electron micrograph, the larger particles, although constituting a major mass fraction (fig. 4), are observed infrequently.

Most of the smaller particles appear to be flakes rather than spherical particles. These flakes are probably oxides which formed during sparking and on standing in the water medium. Similar dispersions of the modified NASA-TRW VI A nickel alloys contained 12 percent oxygen, whereas stoichiometric nickel monoxide (NiO) contains 21.4 percent oxygen. Because of the formation of oxides, therefore, the EDM technique does not necessarily produce material that is more soluble in acids than the bulk metal.

Although these data are self-consistent and reasonably reproducible, they represent effective size distributions only because the particles are nonspherical and therefore do not strictly follow equation (1). They are intended to provide some information on particle characteristics which might aid the analyst in applying the EDM method of sample preparation to various modes of analysis which require the introduction of the dispersions into aspiration systems.

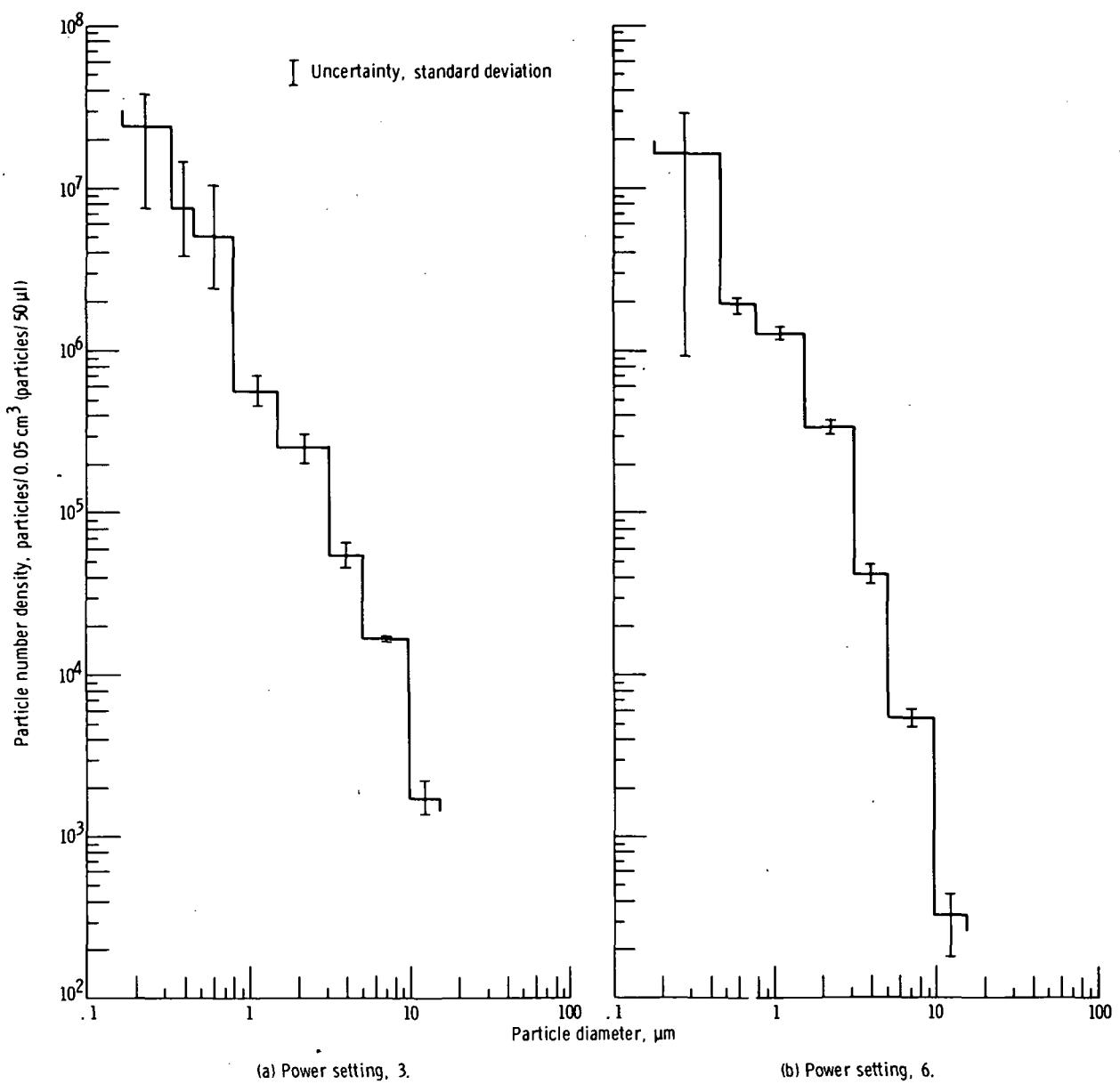


Figure 6. - Particle number distribution in dispersion prepared from nickel-base alloy by EDM.

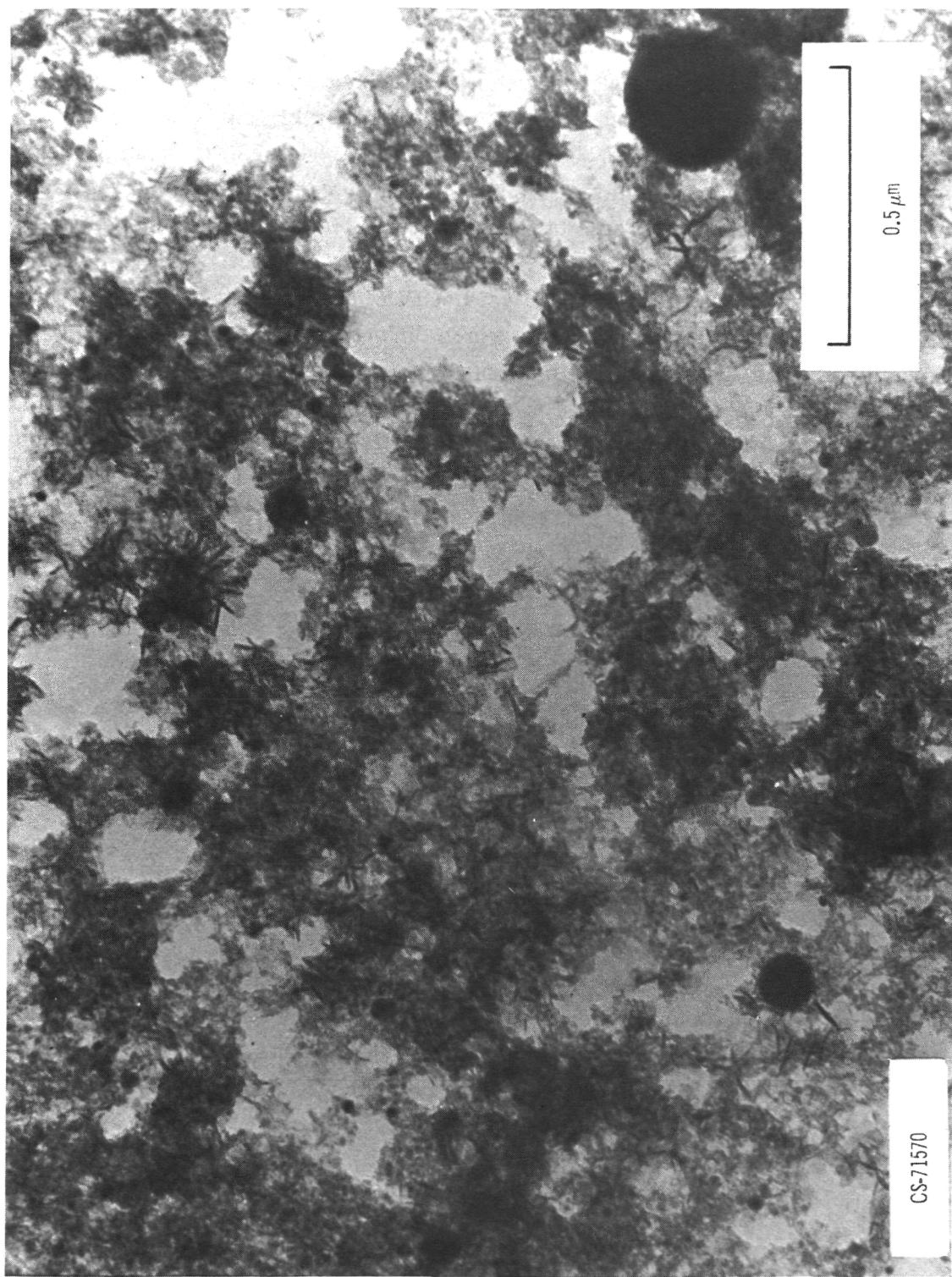


Figure 7. - Scanning electron micrograph of EDM nickel-base alloy. Power setting, 6; temperature, 90 K.

## Spectrochemical Analysis of Dispersions

There are two important questions about the dispersions which relate directly to the usefulness of EDM as a sample preparation procedure. They are (1) to what degree can these dispersions be utilized in analytical systems developed to accommodate true solutions, and (2) to what extent do the small amounts (milligrams) of particulate material represent the chemistry of the parent bulk alloy. An attempt to answer these questions was made by spectrochemical analysis of dispersions produced from several different nickel alloys. A representative sample of the results is reported and discussed in this section.

Arc-excited emission. - The direct analysis of EDM dispersions in water by the arc-excited emission procedure gave results which differed significantly ( $t > 2$ ) from the results obtained from the concurrent analysis of the acid solution of the same alloy specimen. These differences increased for the dispersions produced at the higher EDM spark powers (settings below 4). This trend was established by using Hastelloy C and is shown in figure 8, where the combined analytical errors for the analysis of each disper-

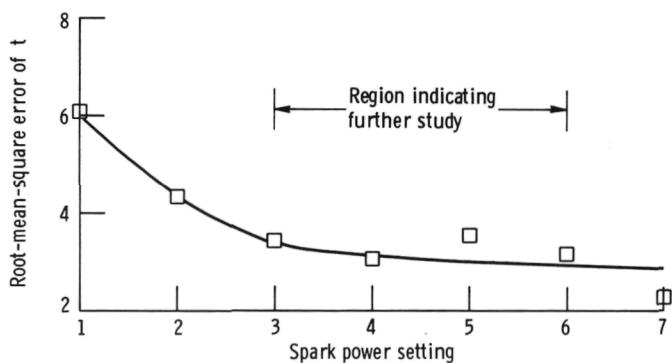


Figure 8. - Root-mean-square errors in spectrochemical analyses of water dispersions of Hastelloy C produced by EDM at various spark powers. Error for acid solution, 0.454  $t$ .

sion are plotted against the spark power setting. The combined analytical error for an analysis is the root mean square of the  $t$  values for all elements analyzed. It is computed by

$$\text{root-mean-square error} = \left( \frac{\sum_{i=1}^n t_i^2}{n - 1} \right)^{1/2}$$

where  $i$  is the analyte element. The trend of increasing errors may have been related to the larger particle sizes which were produced at the higher spark power settings. The larger analysis differences when higher spark power was used may have been caused by particle size effects either in the volumetric sampling step or in the excitation procedure, or both. It was concluded from figure 8 that the optimum spark power setting is 6.

The addition of acid to the dispersions, however, caused the analytical results to agree more closely with the results obtained from acid solutions of the same specimen. With acidified dispersions produced at higher spark powers (settings below 4) the results, though improved, were still unacceptable. The best and only acceptable results for any of the EDM alloy dispersions were obtained by acidification of dispersions produced at the lower spark power (setting of 6).

When acid was added, no attempt was made to dissolve the particulate material completely, and a significant residue usually remained. Examples of results of analyses of acidified dispersions using true acid solutions as standards are given in tables III to V for the three nickel alloys used. The  $t$  values in the tables indicate that the differences between the analyses of acid solutions and the dispersions were not statistically significant.

These results led to the generalization that dispersions produced at low EDM spark power (settings near 6) and having acid added to them will yield analytical results which are not significantly different from those of a concurrent analysis of a true solution of the same specimen.

TABLE III. - SPECTROCHEMICAL ANALYSIS OF NICKEL ALLOY MCRAI  
BY ARC-EXCITED RESIDUE PROCEDURE

Spectrochemical analysis			Relative analytical accuracy			
Element	Acid solution, percent	EDM dispersion, <sup>a</sup> percent	Difference, percent	Standard deviation, percent	Root-mean-square error, percent	Analytical difference, $t$ , rms error
Aluminum	3.40	3.4	0	0.8	4.4	0
Chromium	5.03	5.3	5.4	.6	2.6	2.06
Iron	11.80	11.8	0	.5	1.9	0
Manganese	4.19	3.7	-11.7	4.4	8.1	-1.44
Nickel	74.31	74.6	.4	0	1.1	.35
Titanium	.98	.99	1.0	.7	8.5	.12

<sup>a</sup>Produced at power setting of 6.

VIA powder product

Figure 9. - Microstructure of NASA-TRW VIA alloy.

As-cast VIA

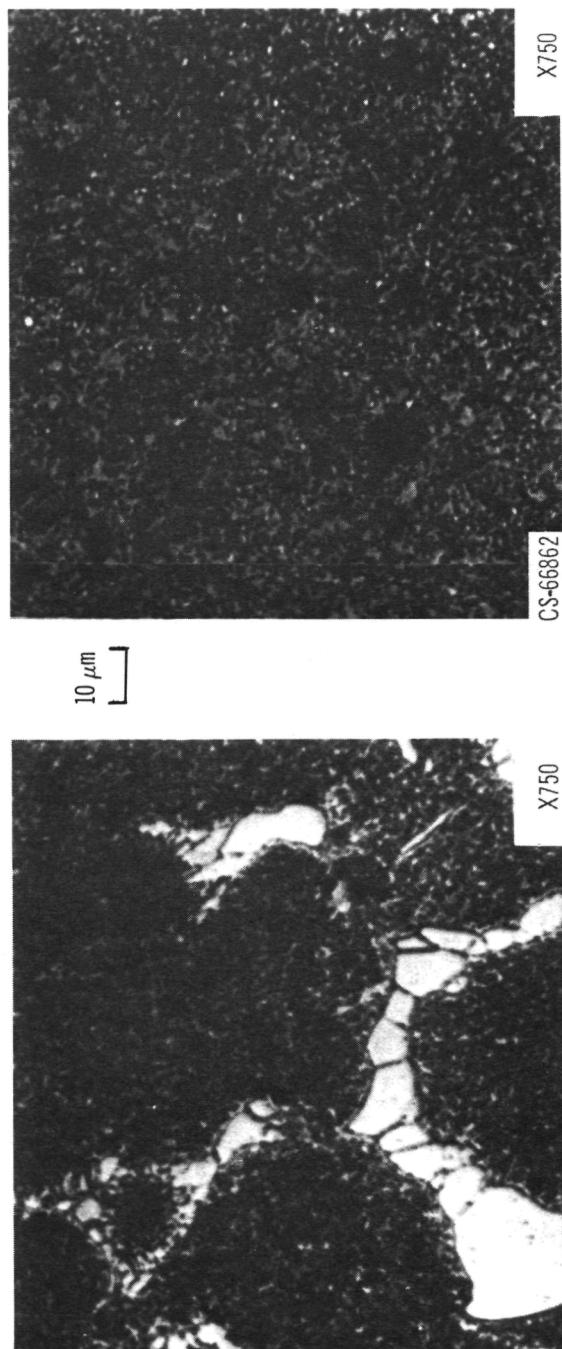


TABLE IV. - SPECTROCHEMICAL ANALYSIS OF CAST NICKEL ALLOY,  
MODIFIED NASA-TRW VI A, BY ARC-EXCITED EMISSION PROCEDURE

Spectrochemical analysis			Relative analytical accuracy			
Element	Acid solution, percent	EDM dispersion, <sup>a</sup> percent	Difference, percent	Standard deviation, percent	Root-mean-square error, percent	Analytical difference, t, rms error
Aluminum	5.18	4.8	-7.3	0.7	5.8	-1.26
Cobalt	7.50	7.9	5.3	.1	5.1	1.05
Chromium	5.74	5.9	2.8	1.2	5.7	.49
Hafnium	.52	.40	-23.1	1.7	20	-1.15
Molybdenum	1.95	2.30	17.9	.3	11.2	1.60
Niobium	.49	.56	14.3	.3	13.3	1.07
Nickel	62.13	62.2	.1	.4	4.3	.03
Tantalum	9.47	9.6	1.4	3.0	8.5	.16
Titanium	.99	.99	0	.3	13.5	0
Tungsten	5.78	5.6	-3.1	.7	6.5	-.48

<sup>a</sup>Produced at power setting of 6.

TABLE V. - SPECTROCHEMICAL ANALYSIS OF POWDER METALLURGY NICKEL ALLOY, MODIFIED NASA-TRW VI A, BY ARC-EXCITED EMISSION PROCEDURE

Spectrochemical analysis			Relative analytical accuracy			
Element	Acid solution, percent	EDM dispersion, <sup>a</sup> percent	Difference, percent	Standard deviation, percent	Root-mean-square error, percent	Analytical difference, t, rms error
Aluminum	4.96	4.8	-3.2	1.5	5.8	-0.56
Cobalt	7.63	7.7	.9	.9	5.1	.18
Chromium	5.65	5.8	2.7	2.4	5.7	.47
Hafnium	.52	.54	3.8	5.8	20	.19
Molybdenum	1.96	1.99	1.5	0	11.2	.14
Niobium	.55	.59	7.3	0	13.3	.55
Nickel	63.27	62.0	-2.0	.1	4.3	-.47
Tantalum	9.12	9.9	8.6	1.6	8.5	1.01
Titanium	1.04	1.20	15.4	4.2	13.5	1.14
Tungsten	5.04	4.7	-6.7	.9	6.5	1.04

<sup>a</sup>Produced at power setting of 6.

The effect of the metallurgical uniformity of the specimen, with respect to microstructure, on the analytical results was determined. Acidified dispersions were produced from both of the modified NASA-TRW alloys used in this study at a power setting of 6. These two nickel alloys had similar chemical compositions but different metallurgical histories. The powder metallurgical process yielded a microstructure that was much more homogeneous than the microstructure of the as-cast version. Figure 9 is a photomicrograph that shows this contrast. The results of the analyses of the two versions of the modified NASA-TRW VI A alloy are shown in tables IV and V. Again, when  $t$  is used as a significance criterion, these results show that neither analysis was significantly affected by the microstructure. We then conclude that the small amount (about 25 mg) of dispersion particulates generated by about 10 minutes of EDM did represent the chemical composition of the specimen, regardless of its metallurgical history.

Atomic absorption. - Absorbance values from flame atomic absorption analyses of several EDM dispersions produced at a spark power setting of 6 are shown in table VI.

TABLE VI. - SUMMARY OF ATOMIC ABSORPTION DATA FROM EDM  
DISPERSION PARTICULATES IN NITROUS  
OXIDE - ACETYLENE FLAME

Element	Concentra-tion, ppm	Acid solution	EDM plus acid	EDM in water
		Absorbance		
Aluminum	50	0.312, 0.312	0.265, 0.260	0.087, 0.091
	5	-----	-----	.019, .018
Molybdenum	20	1.836	2.128	0.230
	2	-----	-----	.048
Chromium	50	2.547	2.402	1.280
	5	-----	-----	.193
Cobalt	70	1.904	1.864	0.840
	7	-----	-----	.170

Although these results are preliminary, they indicate that these dispersions can be aspirated into and excited by the flame source without operational difficulty. They also show concentrational sensitivity and give reasonably reproducible results. In other experiments, dispersions were aspirated into the flame, and the absorbances for aluminum, cobalt, and chromium were repeatable to within about 4 percent, the relative standard deviation. The contribution of nonspecific absorption, caused by the presence of dispersion particulates in the optical path, was minimal in these experiments, as evidenced by the absorbances obtained when elements not present in a given alloy were

measured. Generally, these blank absorbances were comparable to the limit of detection for the element. Although this analytical system yielded results which were reproducible, the desired analytical accuracy was not achieved when acid solutions were used as standards for these analyses. This problem can be circumvented by using EDM dispersions as standards.

Inductively coupled plasma. - Preliminary results were obtained by aspirating several EDM dispersions directly into the excitation plasma. No operational difficulties were encountered in the aspiration, and the emission intensities showed concentrational sensitivity. With these two basic requirements met, an analytical method appears to be feasible with additional development work.

#### CONCLUDING REMARKS

Electric discharge machining has been demonstrated to be a useful sample preparation tool for subsequent chemical analysis. Commercially available table-top machines with servomechanism-controlled spark gaps provide a convenient means for producing dispersions of metals from bulk alloys. The dispersions can be produced at rates between 2 and 10 milligrams per minute. The particulated materials produced from some nickel alloys typically had mass-median diameters of about 3 micrometers, and about 25 percent of the material remained in suspension after 30 hours.

The utility of the EDM sample preparation procedure was demonstrated by the successful analysis of volumes of acidified nickel alloy dispersions of the order of 0.01 cubic centimeter by using an arc-excited spectrochemical procedure. This procedure involved an analytical system which had been calibrated with acid solution standards.

The results also indicate the feasibility of analyzing these dispersions by other spectrochemical methods which require direct aspiration of liquids into flame or plasma sources (e.g., the inductively coupled plasma or flame-excited procedure). However, because of the low efficiency of these systems for vaporizing solid particles, calibrations using dispersions prepared from standard materials probably will be necessary. The further use of EDM as a means of comminution of bulk metals to facilitate acid dissolution and hot salt fusions would also appear useful, but this was not investigated in detail. However, the apparent advantage for acid dissolution afforded by increasing the surface area by EDM was complicated by the partial formation of oxides in the water medium.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, August 6, 1975,  
505-01.

## REFERENCES

1. Gordon, William A.; and Chapman, Gilbert B.: Quantitative Direct-Current Arc Analysis of Random Compositions of Microgram Residues in Silver Chloride Common Matrix. NASA TN D-5532, 1969.
2. Ghiglione, M.; and Eljuri, E.: Metallic Dispersions as Solid Samples in Atomic Absorption. Acta Cientifica Venezolana, vol. 21, no. 3, 1970, pp. 123-124.
3. Scott, R. H.; Fassel, V. A.; Kniseley, R. N.; and Nixon, D. E.: Inductively Coupled Plasma-Optical Emission Analytical Spectrometry. Analy. Chem., vol. 46, no. 1, Jan. 1974, pp. 75-80.
4. Natrella, M. G.: Experimental Statistics. NBS-Handbook-91, Natl. Bureau of Standards, 1963.

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